REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 3-31-96	3. REPORT TYPE AND DATES COVERED FINAL REPORT (2-1-93/1-31-96)

4. TITLE AND SUBTITLE
FINAL REPORT "Non-Linear Optical Effects in Molecules" AFOSR-F49620-93-1-0118

5. FUNDING NUMBERS
61102F
2303/FS

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AFOSR-TR-96
0149

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10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-93-1-0118

19960404 057

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release.
Distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
We analyze the evolution of first principle molecular theory in obtaining reliable values of molecular hyperpolarizabilities. Such quantities place severe demands on the capability of quantum chemistry, as large basis sets, frequency dependence, and high levels of electron correlation are all shown to be essential in obtaining observed, gas phase hyperpolarizabilities to within an error of 10%. *Ab initio* Hartree Fock results are typically in error by nearly a factor of two, while the errors due to the neglect of frequency dependence average ~10–30% depending upon the particular process. It is also shown that for small molecules, standard semi-empirical approaches, like INDO and INDO/S, will often not even give the correct sign for hyperpolarizabilities. It is demonstrated that using state-of-the-art correlated, frequency dependent methods, it is possible to provide results to within 10%. Excluding any one of the essential elements, though, destroys the agreement.

14. SUBJECT TERMS

15. NUMBER OF PAGES
9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 1

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

FINAL REPORT

Non-Linear Optical Effects in Molecules

AFOSR-F49620–93–1–0118

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19 MAR 1996

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Can Quantum Chemistry Provide Reliable Molecular Hyperpolarizabilities?

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In the late 70's, one of us (RJB) became interested in molecular hyperpolarizabilities as the essential element in non-linear optics (NLO) when Gordon Wepfer at the Air Force Office of Scientific Research called attention to J. F. Ward's results from dc-induced second harmonic generation (dcSHG) experiments and the enormity of their discrepancy with theoretical results. Tables I and II are extracted from a slightly later, 1979, paper of Ward and Miller (*1*) demonstrating the problem.

Not only was the existing theory results of the time typically in error by a factor of 3 to 5 in magnitude for the electric susceptibility, $\chi_{\parallel}^{(2)}$, but even the signs were frequently wrong. (The sign is positive if the measured quantity $\mu\chi_{\parallel}^{(2)}$ is positive, where μ is the permanent dipole moment.) When experimental numbers were obtained by other techniques, which should only differ by different dispersion effects that are typically less than 10%; they, too, had little correspondence with the dcSHG data. Note from Table I the -3500 value for NH_3 from refractivity virial data compared to -209±5 for the dcSHG, $\chi_{\parallel}^{(2)}$.

Table I $\chi_{\parallel}^{(2)}$ in units of 10^{-33} esu/molecule. Theoretical values from various molecular orbital calculations — semi-empirical (SE), uncoupled Hartree-Fock (HF), and coupled Hartree-Fock (CHF) — and a single other experimental value are included for comparison. The sign of $\mu\chi_{\parallel}^{(2)}$ is unambiguously determined by the experiment and is independent of the sense chosen for the molecular z axis. This table extracted from J. F. Ward and C. K. Miller (*1*).

	μ^a	$\chi_{\parallel}^{(2)}$ SHG	THEORY			Other EXP
			Semi-Empirical	Uncoupled HF	Coupled HF	
C⁻O⁺	0.112 ±0.005	+129 ±14	-43.5[b] (+95)[d]	+879[c] +420[c] +387[c] -438[e]		

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N⁻O⁺	0.15872 ±0.00002	+147 ±17	+47.7[b]			
H₂⁺S⁻	0.974 ±0.005	-43 ±9				
N⁻H₃⁺	1.474 ±0.009	-209 ±5	56.4[b]		-44.4[f] -65.1[f] -19.0[f] -15.6[h] -40.8[h]	-3500[g]
H₂⁺O⁻	1.86 ±0.02	-94 ±4	120[b]	90.6	-52.5[f] -79.2[f] -21.9[f] -51.6[h] -48.0[h]	

[a] Electric dipole moments in Debye units from Landolt-Bernstein, Zahlenwerte und Funktionen, Neue Serie, Vols. II/4 and II/6 (Springer-Verlag, Berlin) and Ref. 18. The sense of the NO moment is suggested by F. P. Billingsley II, J. Chem. Phys. **63** 2267 (1975); **62**, 864 (1975).

[b] N. S. Hush and M. L. Williams, Theoret. Chim. Acta (Berlin) (*25*), 346 (1972). Signs for NH_3 and H_2O are ambiguous.

[c] J. M. O'Hare and R. P. Hurst, J. Chem. Phys. (*46*), 2356 (1967).

[d] $\chi_{zzz}^{(2)}$ (0;0,0) from A. D. McLean and M. Yoshimine, J. Chem. Phys. (*46*), 3682 (1967).

[e] S. P. Liebmann and J. W. Moskowitz, J. Chem. Phys. **54**, 3622 (1971).

^{f} P. Lazzeretti and R. Zanasi, Chem. Phys. Lett. (*39*), 323 (1976) *Note added in proof.* Recent reconsideration of the sign of these entries yields the negative signs now shown here — P. Lazzeretti (private communication). Overall consistency is substantially improved by this change.

^{g} Refractivity virial data from A. R. Blythe, J. D. Lambert, P. J. Petter and H. Spoel, Proc. R. Soc. (London) A **255**, 427 (1960).

^{h} G. P. Arrighini, M. Maestro and R. Moccia, Symp. Farad. Soc. **2**, 48 (1968).

In Table II, the discrepancy among different experiments is even more apparent for $\chi_\parallel^{(3)}$ compared to other dcSHG values, three wave mixing (TWM), Kerr effect, and third harmonic generation (THG) experiments. The theory is even off by about a factor of 2 from a static value for H_2. The one reasonable theoretical number they cite is our static, correlated value for N_2, one of our first (unpublished), that is beginning to be in reasonable agreement with $\chi_\parallel^{(3)}$.

Table II $\chi_\parallel^{(3)}$ in units of 10^{-39} esu/molecule. Values from other dc-electric field-induced second-harmonic generation (dcSHG), three-wave mixing (TWM), Kerr effect, and third-harmonic generation (THG) experiments, along with theoretical results, are included for comparison. This table extracted from J. F. Ward and C. K. Miller (1).

	$\chi_\parallel^{(3)}$					
	dcSHG Ward & Miller	*dcSHG[a]*	*TWM[b]*	*Kerr*	*THG[c]*	*Theory*
H_2	65.2 ±0.8	79	-	47[d] ±5	80 ±12	34[e]
N_2	86.6 ±1.0	-	104	120[f] ±10	107 ±17	71[g]
O_2	95.3 ±1.6	110	100	-	-	-
CO_2	111.9 ±1.3	-	192	750[f] ±160	156 ±23	
CO	144 ±4	-	138	-	-	-
NO	235 ±7	-	322	-	-	-
H_2S	865 ±22	-	-	-	-	-
NH_3	511 ±9	-	-	-	-	-
H_2O	194 ±10	-	-	-	-	-

[a] Data from G. Mayer, C. R. Acad. Sci. **B276**, 54 (1968) and G. Hauchecorne, F. Kervervé and G. Mayer, J. Phys. (Paris) **32**, 47 (1971), normalized using the dcSHG coefficient for argon from R. S. Finn and J. F. Ward, Phys. Rev. Lett. **26**, 285 (1971).

[b] Data from W. G. Rado, Phys. Lett. **11**, 123 (1967), normalized using the dcSHG coefficient for argon from R. S. Finn and J. F. Ward, Phys. Rev. Lett. *26*, 285 (1971).

[c] J. F. Ward and G. H. C. New, Phys. Rev. *185*, 579 (1969).

[d] A. D. Buckingham and B. J. Orr, Proc. R. Soc. (London) A**305**, 259 (1968).

[e] χ_{zzzz} (0;0,0,0) from A. D. McLean and M. Yoshimine, J. Chem. Phys. **46**, 3682 (1967).

[f] A. D. Buckingham, M. P. Bogard, D. A. Dunmur, C. P. Hobbs and B. J. Orr, Trans. Fora. Soc. **66**, 1548 (1970).

[g] χ_{zzzz} (0;0,0,0) from R. J. Bartlett and G. D. Purvis (private communication).

This chapter, which is intended to be useful to experimentalists who are trying to assess the reliability of the theory, but also to theoreticians, as it provides an overview of the theory which can and has been used, addresses the demands that hyperpolarizabilities place on first-principle *ab initio* electronic structure theory; and the level required for the adequate evaluation of molecular hyperpolarizabilities. After

doing some basic elementary perturbation theory that underlies all that is done, and which provides definitions and a framework for discussion, we will explain the various levels of quantum chemical application, illustrated by numerical results we have obtained that emphasize the various approximations employed in electronic structure in its application to hyperpolarizabilities. We will also demonstrate how the theory has necessarily evolved to provide a realistic treatment of such properties.

The order of presentation will follow our own odyssey that led us to introduce electron correlation into molecular hyperpolarizabilities (2,3), using, then new, many-body perturbation theory (MBPT) methods (4,5); to make a prediction for the FH molecule, that had later ramifications (6,7); to use new coupled-cluster (CC) correlated methods including those augmented by triples (8,9); to explore vibrational polarizabilities in static electric fields (10); and to introduce frequency dependence by developing analytical derivative time-dependent Hartree Fock (TDHF) theory (11,12). The latter, which enables a first (decoupled) treatment of both the essential frequency dependent and correlation aspects of the problem (13), culminates in a uniform study of ten molecules (14). The correlation calculations were assisted by parallel developments in analytical derivative CC/MBPT theory (15–18). Finally, we coupled correlation and frequency dependence in the new equation-of-motion (EOM) CC method for hyperpolarizabilities (19,20). By taking this evolutionary viewpoint, we hope the current review will complement the other recent excellent reviews (21–23) on the topic.

The theory also offers different, conceptual viewpoints on hyperpolarizability evaluation and interpretation, and this degree of flexibility should be better appreciated when comparing theoretical numbers and addressing NLO design criteria. We will conclude with some recommendations for some future developments in the continuing evaluation of predictive quantum chemical methods for NLO material design.

Perturbation Theory of Molecular Hyperpolarizabilities

The quantities of interest are the electric susceptibilities $\chi_{\parallel}^{(2)}$ and $\chi_{\parallel}^{(3)}$. In the gas phase experiments of interest here, there is no particular distinction between macroscopic and microscopic susceptibilities and the hyperpolarizabilities, as they are simply related. Those of particular interest are obtained from electric field (dc) induced second harmonic generation experiments (1). Namely, a sample of gas is subjected to a dc field (ε_o) and an optical electric field $\varepsilon_\omega(e^{i\omega t} + e^{-i\omega t})$ at frequency ω, to induce a dipole moment at frequency 2ω. Allowing for the various manipulations required to relate the molecular quantities to the laboratory fixed observables,

$$\vec{\mu}^{2\omega} = \frac{3}{2}\chi_{\parallel}^e(-2\omega; o, \omega, \omega)\varepsilon_o\varepsilon_{\omega o}^2$$

$$\chi_{\parallel}^e(-2\omega; o, \omega, \omega) = \chi_{\parallel}^{(3)}(-2\omega; o, \omega, \omega) + \frac{\vec{\mu}}{9KT}\chi_{\parallel}^{(2)}(-2\omega; \omega, \omega)$$

(1)

$\chi_{\parallel}^{(2)}(-2\omega; \omega, \omega)$ for second harmonic generation (SHG) is separated from $\chi_{\parallel}^{(3)}(-2\omega; o, \omega, \omega)$, which is dcSHG, by studying $\vec{\mu}^{2\omega}$ as a function of T. Numbers

relative to a standard, typically He gas, are obtained. Revisions of the He reference value cause some slight rescaling of the experimental numbers (22). Furthermore, we relate the susceptibilities to the molecular hyperpolarizabilities via,

$$
\begin{aligned}
\chi_{\parallel}^{(2)}(-2\omega; \omega, \omega) &= \beta_{\parallel}(-2\omega; \omega, \omega)/2 \\
&= \frac{1}{2}\Big[(\beta_{iij} + \beta_{iji} + \beta_{jji})/5\Big] \\
\chi_{\parallel}^{(3)}(-2\omega; o, \omega, \omega) &= \gamma_{\parallel}(-2\omega; o, \omega, \omega)/6 \\
&= \frac{1}{6}\Big[(\gamma_{iijj} + \gamma_{ijji} + \gamma_{ijij})/15\Big]
\end{aligned}
\tag{2}
$$

where the Einstein summation convention is employed, meaning all repeated indices are summed, i.e. $\vartheta_{ii} = \vartheta_{xx} + \vartheta_{yy} + \vartheta_{zz}$. The parallel designation ($\parallel$) means measured parallel to the dc field, while the ($\perp$) component can be similarly obtained. As $\beta_{\parallel}$ and $\gamma_{\parallel}$ are properties of molecules, they constitute the objective for first-principle quantum mechanical evaluation; the subject of this chapter.

The basic idea underlying any treatment of a molecular response to an electric field, static or oscillatory, is the solution of the molecular Schrödinger equation in the presence of the field. We will first consider the static case, generalizing the approach for frequency dependence in Section 7. Our perturbation $\vec{\varepsilon}_o \cdot \vec{W} = \vec{\varepsilon}_o \cdot \sum_i e_i \vec{r}_i$ is given by the interaction of an electron e_i at position $\vec{r}_i$ with a static electric field,

$$
\vec{\mathcal{E}}_o = \varepsilon_{xo}\hat{i} + \varepsilon_{yo}\hat{j} + \varepsilon_{zo}\hat{k},
\tag{3}
$$

where ε_{xo}, ε_{yo}, and ε_{zo} are the field strengths in the x, y, and z directions of magnitude $|\varepsilon|$. In atomic units, e becomes minus unity, so we have a Hamiltonian,

$$
\mathcal{H}(\vec{\varepsilon}_o) = \mathcal{H}_o + \vec{\varepsilon}_o \cdot \vec{W} = \mathcal{H}_o - \vec{\varepsilon}_o \cdot \sum_i \vec{r}_i,
\tag{4}
$$

where H_o consists of the usual kinetic energy, $-\frac{1}{2}\sum_i \nabla_2^2$ and potential energy, $-\sum_{\alpha,i} \frac{Z_\alpha}{r_{\alpha i}} + \frac{1}{2}\sum_{i,j} \frac{1}{r_{ij}} + \frac{1}{2}\sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}$, composed of the electron nuclear attraction, the two-electron, electron-electron repulsion operator, and the proton-proton repulsion. Greek letters indicate atoms and i,j electrons. W contains the negative sign. The solution to the time independent Schrödinger equation

$$
\mathcal{H}_o \psi_k^o = E_k^o \psi_k^o
\tag{5}
$$

provides the ground, $\psi_o = \psi_o^o$ and excited states, $\{\psi_k^o\}$, and associated eigenvalues, $\{E_k^o\}$, for the unperturbed molecule. Notice these are the exact, many-particle unperturbed states.

We now seek a solution for the perturbed Hamiltonian in its ground state

$$
\mathcal{H}(\vec{\varepsilon}_o)\Psi(\vec{\varepsilon}_o) = E(\vec{\varepsilon}_o)\Psi(\vec{\varepsilon}_o)
\tag{6}
$$

The natural way to attempt a solution is perturbation theory. Hence, we expand, $\mathcal{H}(\vec{\varepsilon}_o)$, $\Psi(\vec{\varepsilon}_o)$ and $E(\vec{\varepsilon}_o)$ in a perturbation series in $\vec{\varepsilon}_o$. For the time being, we will assume the field lies solely in the z direction, so $\varepsilon_{xo} = \varepsilon_{yo} = 0$ and $\varepsilon_{zo} = \varepsilon_o$. Then,

$$
(H_o + \varepsilon_o W)\left(\psi_o + \varepsilon_o \psi^{(1)} + \varepsilon_o^2 \psi^{(2)} + \varepsilon_o^3 \psi^{(3)} + \ldots\right)
$$
$$
= \left(E + \varepsilon_o E^{(1)} + \varepsilon_o^2 E^{(2)} + \ldots\right)\left(\psi_o + \varepsilon_o \psi^{(1)} + \ldots\right)
\tag{7}
$$

As the equality has to be true for any power of ε_o (i.e. all quantities are linearly independent), gathering terms of a given power of ε_o together, we obtain for ε_o^1;

$$
(E_o - \mathcal{H}_o)\psi^{(1)} = \left(W - E^{(1)}\right)\psi_o
\tag{8}
$$

for ε_o^2

$$
(E_o - \mathcal{H}_o)\psi^{(2)} = \left(W - E^{(1)}\right)\psi^{(1)} - E^{(2)}\psi_o
\tag{9}
$$

for ε_o^3

$$
(E_o - \mathcal{H}_o)\psi^{(3)} = \left(W - E^{(1)}\right)\psi^{(2)} - E^{(3)}\psi_o - E^{(2)}\psi^{(1)}
\tag{10}
$$

and for ε_o^4

$$
(E_o - \mathcal{H}_o)\psi^{(4)} = \left(W - E^{(1)}\right)\psi^{(3)} - E^{(4)}\psi_o - E^{(3)}\psi^{(1)} - E^{(2)}\psi^{(2)}
\tag{11}
$$

These are sufficient to take us through the electronic dipole moment, $\underline{\mu}$, the dipole polarizability tensor, $\underline{\alpha}$, and the β and γ, hyperpolarizability tensors. Multiplying on the left by $\langle\psi_o|$, and using the fact that $\langle\psi_o|(E_o - \mathcal{H}_o) = 0$, we have

$$
E^{(1)} = \langle\psi_o|W|\psi_o\rangle
\tag{12}
$$

Similarly, we obtain

$$
E^{(2)} = \langle\psi_o|\left(W - E^{(1)}\right)|\psi^{(1)}\rangle = \langle\psi_o|W|\psi^{(1)}\rangle
$$
$$
E^{(3)} = \langle\psi_o|W|\psi^{(2)}\rangle = \langle\psi^{(1)}|W - E^{(1)}|\psi^{(1)}\rangle
\tag{13}
$$
$$
E^{(4)} = \langle\psi_o|W|\psi^{(3)}\rangle = \langle\psi^{(2)}|E_o - \mathcal{H}_o|\psi^{(2)}\rangle - E^{(2)}\langle\psi^{(1)}|\psi^{(1)}\rangle
$$

where we have used the intermediate normalization condition, $\langle\psi_o|\psi^{(m)}\rangle = 0$ for $m \neq 0$. The second form comes from manipulations that demonstrate the 2n+1 rule that an nth order wavefunction will determine E^{2n+1} and the analogous 2n rule for even orders.

Instead of straightforward perturbation theory, we can also derive these formulae from explicit differentiation of the expectation value of $\Psi(\varepsilon_o)$ with respect to ε_o. From equation 6, we have the expectation value,

$$
E(\varepsilon_o)\langle\Psi(\varepsilon_o)|\Psi(\varepsilon_o)\rangle = \langle\Psi(\varepsilon_o)|\mathcal{H}(\varepsilon_o)|\Psi(\varepsilon_o)\rangle
\tag{14}
$$

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and differentiation gives,

$$\left\langle \Psi(\varepsilon_o) \left| (\mathcal{H}(\varepsilon_o) - E(\varepsilon_o)) \right| \frac{\partial \Psi}{\partial \varepsilon_o} \right\rangle + \left\langle \frac{\partial \Psi}{\partial \varepsilon_o} \left| (\mathcal{H}(\varepsilon_o) - E(\varepsilon_o)) \right| \Psi(\varepsilon_o) \right\rangle$$
$$= \left\langle \Psi(\varepsilon_o) \left| \frac{\partial H}{\partial \varepsilon_o} - \frac{\partial E}{\partial \varepsilon_o} \right| \Psi(\varepsilon_o) \right\rangle \tag{15}$$

As we want to evaluate this at $\varepsilon_o = 0$, using $(\mathcal{H}_o - E_o)|\psi_o\rangle = 0$, and its complex conjugate (c.c.), gives

$$\frac{\partial E}{\partial \varepsilon_o}\bigg]_{\varepsilon_o=0} = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \psi_o \right\rangle\bigg]_{\varepsilon_o=0} = \left\langle \psi_o \left| W \right| \psi_o \right\rangle \tag{16}$$

This is simply a statement of the simple Hellman-Feynmann theorem that the derivative of the energy is given as the expectation value of $\frac{\partial \mathcal{H}}{\partial \varepsilon_o}$.

If we proceed to the higher derivatives, we will obtain

$$\frac{\partial^2 E}{\partial \varepsilon_o^2}\bigg]_{\varepsilon_o=0} = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} - \frac{\partial E}{\partial \varepsilon_o} \right| \frac{\partial \psi}{\partial \varepsilon_o} \right\rangle + \text{c.c.} = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \frac{\partial \psi}{\partial \varepsilon_o} \right\rangle + \text{c.c.} \tag{17}$$

or

$$\frac{1}{2}\frac{\partial^2 E}{\partial \varepsilon_o^2}\bigg]_{\varepsilon_o=0} = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \frac{\partial \psi}{\partial \varepsilon_o} \right\rangle \tag{18}$$

In third and fourth order,

$$\frac{1}{3!}\frac{\partial^3 E}{\partial \varepsilon_o^3}\bigg]_{\varepsilon_o=0} = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \frac{1}{2!}\frac{\partial^2 \psi}{\partial \varepsilon_o^2} \right\rangle = \left\langle \frac{\partial \psi}{\partial \varepsilon_o} \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} - \frac{\partial E}{\partial \varepsilon_o} \right| \frac{\partial \psi}{\partial \varepsilon_o} \right\rangle$$
$$\frac{1}{4!}\frac{\partial^4 E}{\partial \varepsilon_o^4}\bigg]_{\varepsilon_o=0} = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \frac{1}{3!}\frac{\partial^3 \psi}{\partial \varepsilon_o^3} \right\rangle \tag{19}$$

Clearly, this is simply perturbation theory, since up to a numerical factor, $\psi^{(1)} = \frac{\partial \psi}{\partial \varepsilon_o}$, $E^{(1)} = \frac{\partial E}{\partial \varepsilon_o}$, $\psi^{(2)} = \frac{1}{2}\frac{\partial^2 \psi}{\partial \varepsilon_o^2}$, $E^{(2)} = \frac{1}{2}\frac{\partial^2 E}{\partial \varepsilon_o^2}$, etc. In other words, we use a McLaurin's series expansion for E, $E(\varepsilon_o) = E_o + \frac{\partial E}{\partial \varepsilon_o}\varepsilon_o + \frac{1}{2!}\frac{\partial^2 E}{\partial \varepsilon_o^2}\varepsilon_o^2 + \frac{1}{3!}\frac{\partial^3 E}{\partial \varepsilon_o^3}\varepsilon_o^3 + \dots$ and Ψ, instead of a straight perturbation series, which introduces the numerical factors that relate the perturbative energies to the derivatives $E^{(n)} = \frac{1}{n!}\frac{\partial^n E}{\partial \varepsilon_o^n}$.

We now define the electric properties as the electric dipole in the z direction:

$$\frac{\partial E}{\partial \varepsilon_o} = -\mu_z = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \psi_o \right\rangle = \left\langle \psi_o \left| W \right| \psi_o \right\rangle = E^{(1)} \tag{20}$$

the dipole polarizability;

$$\frac{\partial^2 E}{\partial \varepsilon_o^2} = -\alpha_{zz} = \left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \frac{\partial \psi}{\partial \varepsilon_o} \right\rangle = 2\left\langle \psi_o \left| W \right| \psi^{(1)} \right\rangle = 2E^{(2)} \tag{21}$$

the first hyperpolarizability;

$$\frac{\partial^3 E}{\partial \varepsilon_o^3} = -\beta_{zzz} = 3\left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \frac{\partial^2 \psi}{\partial \varepsilon_o^2} \right\rangle = 3!\left\langle \psi_o \left| W \right| \psi^{(2)} \right\rangle = 3!E^{(3)} \tag{22}$$

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and the second hyperpolarizability;

$$\frac{\partial^4 E}{\partial \varepsilon_o^4} = -\gamma_{zzzz} = 4\left\langle \psi_o \left| \frac{\partial \mathcal{H}}{\partial \varepsilon_o} \right| \frac{\partial^3 \psi}{\partial \varepsilon_o^3} \right\rangle = 4! \left\langle \psi_o \left| W \right| \psi^{(3)} \right\rangle = 4! E^{(4)} \qquad (23)$$

That is,

$$E(\varepsilon_o) = E_o - \mu_z \varepsilon_{zo} - \frac{1}{2!}\alpha_{zz}\varepsilon_{zo}^2 - \frac{1}{3!}\beta_{zzz}\varepsilon_{zo}^3 - \frac{1}{4!}\gamma_{zzzz}\varepsilon_{zo}^4 + \ldots \qquad (24)$$

which gives the well known series.

More generally, when all components are considered, with the Einstein summation convention, we have

$$E = E - \mu_i \varepsilon_{io} - \frac{1}{2!}\alpha_{ij}\varepsilon_{io}\varepsilon_{jo} - \frac{1}{3!}\beta_{ijk}\varepsilon_{io}\varepsilon_{jo}\varepsilon_{ko} - \frac{1}{4!}\gamma_{ijkl}\varepsilon_{io}\varepsilon_{jo}\varepsilon_{ko}\varepsilon_{lo} - \ldots \qquad (25)$$

or for the induced dipole moment,

$$\mu_i(\varepsilon_o) = \mu_i(o) + \alpha_{ij}\varepsilon_{jo} + \frac{1}{2!}\beta_{ijk}\varepsilon_{jo}\varepsilon_{ko} + \frac{1}{3!}\gamma_{ijkl}\varepsilon_{jo}\varepsilon_{ko}\varepsilon_{lo} + \ldots \qquad (26)$$

Whether the numerical factors are included determines the choice of conventions for polarizabilities. Ward and co-workers use the perturbative definition, meaning that $E^{(2)} = \underline{\alpha}$, $E^{(3)} = \underline{\beta}$, and $E^{(4)} = \underline{\gamma}$, e.g., while the power series choice directly associates the derivatives with the polarizabilities, obviating the numerical factors. Since this choice has direct correspondence with the energy derivatives, it appeals more to theoreticians.

To evaluate the polarizabilities, we require a knowledge of the perturbed wavefunctions (wavefunction derivatives). It is convenient to introduce the resolvent operator,

$$R_o = (E_o - \mathcal{H}_o)^{-1}Q \qquad (27)$$

where Q represents the projector $(Q^2=Q)$ of all functions orthogonal to the unperturbed reference, ψ_o. *One* such set consists of all other eigenfunctions of H_o (discrete and continuous), making $Q = \sum_{k \neq o} \left| \psi_k^{(o)} \right\rangle\left\langle \psi_k^{(o)} \right|$. For this particular set, $R_o|\psi_k^o\rangle = \left(E_o - E_k^{(o)}\right)^{-1}|\psi_k^o\rangle Q = Q\left(E_o - E_k^{(o)}\right)^{-1}|\psi_k^{(o)}\rangle$. By virtue of excluding ψ_o, the inverse R_o operator is well defined. In terms of the resolvent,

$$\psi^{(1)} = R_o\left(W - E^{(1)}\right)\psi_o = R_o W \psi_o$$
$$\psi^{(2)} = R_o\left(W - E^{(1)}\right)\psi^{(1)} \qquad (28)$$
$$\psi^{(3)} = R_o\left(W - E^{(1)}\right)\psi^{(2)} - R_o E^{(2)}\psi^{(1)}$$

etc., showing that all order wavefunctions are *recursively* computed from the prior ones. Knowing these solutions, we can compute the energy from

$$E^{(n+1)} = \langle \psi_o|W|\psi^{(n)} \rangle \qquad (29)$$

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or explicitly, in a few cases,

$$E^{(2)} = \langle \psi_o | W R_o W | \psi_o \rangle$$

$$E^{(3)} = \langle \psi_o | W R_o \left(W - E^{(1)} \right) R_o W | \psi_o \rangle$$

$$E^{(4)} = \langle \psi_o | W R_o \left(W - E^{(1)} \right) R_o \left(W - E^{(1)} \right) R_o W | \psi_o \rangle - E^{(2)} \langle \psi_o | W R_o^2 W | \psi_o \rangle$$

$$(30)$$

etc.

The particular choice of expansion of $\psi^{(n)}$ in the set of eigenfunctions of H_o leads to the well known sum-over-state (SOS) formulas for the z components,

$$-\mu_z = \langle \psi_o | \hat{z} | \psi_o \rangle \tag{31a}$$

$$-\alpha_{zz} = \sum_{k \neq o} \frac{\langle \psi_o | \hat{z} | \psi_k^{(o)} \rangle \langle \psi_k^{(o)} | \hat{z} | \psi_o \rangle}{E_o - E_k^{(o)}} \tag{31b}$$

$$-\beta_{zzz} = \sum_{k,l \neq o} \frac{\langle \psi_o | \hat{z} | \psi_k^{(o)} \rangle \langle \psi_k^{(o)} | \hat{z} - \langle \psi_o | \hat{z} | \psi_o \rangle | \psi_l^{(o)} \rangle \langle \psi_l^{(o)} | \hat{z} | \psi_o \rangle}{\left(E_o - E_k^{(o)} \right) \left(E_o - E_l^{(o)} \right)} \tag{31c}$$

$$-\gamma_{zzzz} = \sum_{k,l,m \neq o} \frac{\langle \psi_o | \hat{z} | \psi_k^{(o)} \rangle \langle \psi_k^{(o)} | \hat{z} - \langle \psi_o | \hat{z} | \psi_o \rangle | \psi_l^{(o)} \rangle \langle \psi_l^{(o)} | \hat{z} - \langle \psi_o | \hat{z} | \psi_o \rangle | \psi_m^{(o)} \rangle \langle \psi_m^{(o)} | \hat{z} | \psi_o \rangle}{\left(E_o - E_k^{(o)} \right) \left(E_o - E_l^{(o)} \right) \left(E_o - E_m^{(o)} \right)}$$

$$+ \alpha_{zz} \frac{\langle \psi_o | \hat{z} | \psi_k^{(o)} \rangle \langle \psi_k^{(o)} | \hat{z} | \psi_o \rangle}{\left(E_o - E_k^{(o)} \right)^2}$$

$$(31d)$$

The other tensor elements are obtained from exchanging x and y with z in all distinct ways. Henceforth, we will recognize that all practical molecular quantum chemical calculations employ a finite, discrete basis set, so from the beginning we are limited to this choice, and we need not consider any continuum.

Evaluation of Static Hyperpolarizabilities

From the above, it should be abundantly clear that in a basis the derivative approach, equations 20 to 23, and the SOS expressions, equation 31, are simply two equivalent ways of expressing polarizabilities. Furthermore, considering that the choice of excited eigenfunctions of $\mathcal{H}_o$ is just one choice for a complete set representation of the perturbed wavefunctions, $\{\psi^{(n)}\}$, the above SOS forms probably attract more significance in NLO than warranted. For example, since $E_o - E_k^{(o)}$ is the excitation energy, and since $\langle \psi_o | \hat{z} | \psi_k^{(o)} \rangle$ is the z-component of the transition moment, it should be possible to evaluate α_{zz} from equation 31b purely from experiment by knowing *all* electronic excitation energies and transition moments (including those for the continuum in the exact case). The problem is knowing them all—a very large number! Instead, attempts to estimate the SOS by the *few* known excitation energies and

transition moments is likely to be very far from the true value (see our contribution later in this volume (24)). Note for the ground state, all contributions to α_{zz} from $\psi_k^{(o)}$ have the same sign, so there is no potential cancellation among the neglected contributions. The problem is further compounded for β_{zzz} and γ_{zzzz}, where in addition to transition moments from the ground to excited states, it is necessary to know the transition moments relating two excited states, and that information is hard to obtain. Note that β_{zzz} can have either sign. γ_{zzzz} also can have either sign, since although the lead term corresponds to $\langle \psi_o^{(2)} | E_o - \mathcal{H}_o | \psi_o^{(2)} \rangle$ which must be negative (giving a positive contribution to γ_{zzzz}), the second term is positive, attenuating the value of γ_{zzzz}. Lacking a proof that the magnitude of one must be greater than the other, either sign is possible.

From the above we have two viewpoints on the evaluation of static polarizabilities. We can either evaluate energy derivatives of the Schrödinger equation in the presence of the perturbation, or attempt some approximation to the SOS. Obviously, the former does not require any truncation. (As we will see in Section 8 later, with *proper handling* neither does the finite basis SOS.) The simplest recipe for evaluation of the derivatives is to use what is called the finite-field technique. That simply means solve the Schrödinger equation in the presence of the perturbation by choosing a small finite value for ε_o of 0.001 a.u., e.g. Adding an electric field quantity to H_o gives an unbounded $H(\varepsilon_o)$ operator, and if we obtain its exact solution, the lowest energy state would be the field ionized state, a molecular cation plus an electron; but in practice we must use a finite basis set for its solution which is effectively like putting the molecule into a box, and this gives a valid $E(\varepsilon_o)$. Repeating the procedure at $\varepsilon_o = -0.001$, we could obtain the dipole from the numerical derivative,

$$-\mu_z = \frac{\partial E}{\partial \varepsilon_o} = \lim_{\varepsilon_o \to o} \frac{E(\varepsilon_o) - E(-\varepsilon_o)}{2\varepsilon_o} \tag{32}$$

The accuracy depends upon the size of the finite field strength. If it is too large, the numerical derivative is not very accurate, while if too small, there is not a numerically significant change in $E(\varepsilon_o)$.

To obtain all $\underline{\mu}$, $\underline{\alpha}$, $\underline{\beta}$ and $\underline{\gamma}$, we need several more points, so we obtain expressions like

$$\beta_{iii}\varepsilon_{io}^3 = \frac{1}{2}\Big[E(2\varepsilon_{io}) - E(-2\varepsilon_{io})\Big] + \Big[E(\varepsilon_{io}) - E(-\varepsilon_{io})\Big] + \mathcal{O}\big(\varepsilon_o^5\big)$$
$$\gamma_{iiii}\varepsilon_{io}^4 = 4\Big[E(\varepsilon_{io}) + E(-\varepsilon_{io})\Big] - \Big[E(2\varepsilon_{io}) - E(-2\varepsilon_{io})\Big] - 6E(o) + \mathcal{O}\big(\varepsilon_o^6\big) \tag{33}$$

See (2) for others. Note each expression is accurate to the next odd (even) order since only $\underline{\alpha}$, $\underline{\gamma}$, $\underline{\varepsilon}$ and $\underline{\mu}$, $\underline{\beta}$, $\underline{\delta}$ are interrelated (2). This exclusion of the next higher-order contribution greatly helps the precision of such a calculation. However, note that the energy needs to be accurate to a couple of significant digits better than ε_{io}^3 if we are to get β_{iii}. That is, if $\varepsilon_{io} = 0.001$, we require energies to be 10^{-11}. If $\varepsilon_{io} = 0.01$, we would require at least 10^{-8}. For γ_{iiii}, we would need 10^{-10} to 10^{-14}. As molecular integrals in quantum chemical calculations are seldom much more accurate

than 10^{-12}, not to mention other parts of the calculation, finite field procedures for hyperpolarizabilities can raise serious precision problems.

Another problem lies in the proliferation of tensor elements in $\underline{\beta}$ and $\underline{\gamma}$. *Many* energy calculations involving field strengths in different directions are required to evaluate all the numerical derivatives, and at higher levels of sophistication these are quite expensive calculations.

The solution to the above problem is to *analytically* evaluate the derivatives. The simplest is $-\mu_z = \langle \psi_o | \hat{z} | \psi_o \rangle$, which is just an expectation value. For the others, *analytical* means that while solving the Schrödinger equation for E, we also directly obtain all components of the derivatives, $\frac{\partial E}{\partial \vec{\varepsilon}_o}$, $\frac{\partial^2 E}{\partial \vec{\varepsilon}_o \partial \vec{\varepsilon}_o}$, $\frac{\partial^3 E}{\partial \vec{\varepsilon}_o \partial \vec{\varepsilon}_o \partial \vec{\varepsilon}_o}$, etc. in about an equivalent amount of time. This means we differentiate *before* evaluation by using equations 20 to 23 and the explicit solutions for the wavefunctions and derivatives, which are proportional to the perturbed wavefunctions given in equation 28. In a substantial formal and computational achievement of 30 years duration, primarily fueled by the necessity of analytical gradients for atomic displacements in molecules (*15,25,26*), such analytical procedures have been developed in quantum chemistry. Their limitation is that they have not been implemented for all methods. For example, *any-order* analytical higher derivatives with respect to electric field perturbations have been developed for the Hartree-Fock treatment of hyperpolarizabilities by exploiting the recursive nature of perturbation theory (*11,27*), equations 28, 29. For correlated methods, analytical second-order perturbative theory, [MBPT(2)], derivatives are available for $\underline{\alpha}$ and $\underline{\beta}$ (*15*). For other methods, even including highly sophisticated correlated methods like coupled-cluster theory (*28*), the induced dipole $\mu(\vec{\varepsilon}_o)$ can be evaluated analytically, from which numerical derivatives provide $\underline{\alpha}$, $\underline{\beta}$, and $\underline{\gamma}$ (*13*). In this way, at least one ε_o or two to three orders of magnitude is gained in the precision of $\underline{\beta}$ and $\underline{\gamma}$.

Note that equation 31 represents *analytical* expressions, too, since no finite field is involved in their evaluation. The latter viewpoint leads to the analytical evaluation of the (dynamic) polarizability using the equation-of-motion (EOM) CC method (*20*). Obviously, it would be ideal to be able to analytically evaluate third and fourth derivatives using such powerful CC correlated methods, but the theory and implementation has not yet been developed.

Basis Sets and Hartree-Fock Theory

Now that we know a way to calculate a static hyperpolarizability, we can consider other aspects of the calculation. The first approximation to consider is Hartree-Fock (HF), self-consistent field (SCF) theory. That is, we evaluate the energy and its derivatives for the perturbed Hamiltonian by obtaining the energetically best (lowest) single determinant solution, $\Phi_o = \mathcal{A}(\varphi_1(1), \varphi_2(2) \cdots \varphi_n(n))$, to approximate ψ_o. In the absence of $\varepsilon_o W$, that means $E_{\text{HF}} = \langle \Phi_o | H_o | \Phi_o \rangle$, and further, $\mathcal{H}_o \simeq H_o = \sum_{k=1}^{N} f(i)$

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where $f = h + v^{eff}$ and $v^{eff}(1) = \sum_{j=1}^{N} \int \varphi_j(2)\frac{1-P_{12}}{r_{12}}\varphi_j(2)\mathrm{d}\tau$. The effective one-particle operator $v^{eff}(1)$ is an average over the two-particle part. The orbitals $\{\varphi_j\}$ are the solutions $f(1)\varphi_j(1) = \epsilon_j\varphi_j(1)$ where ϵ_j is the HF-SCF orbital energy (not electric field ε or $\underline{\epsilon}$ hyperpolarizability!). Self-consistency is required by ensuring that the orbitals $\{\varphi_j\}$ used in $v^{eff}(1)$ in f are self-consistent with the solutions. This model provides the usual molecular orbital (MO) approximation that underlies much of our conceptual understanding of molecules. This averaging procedure introduces the correlation error, which pertains to electrons' instantaneous interaction that keeps them apart. It corresponds to the perturbation $V = \sum_{i,j}\frac{1}{r_{ij}} - \sum_{i} v^{eff}(i)$, which we will consider later in Section 6. The full Hamiltonian of equation 41 is thus $\mathcal{H} = H_o + \varepsilon_o W + V$.

The simplest way to consider doing a HF calculation of a polarizability is the finite-field procedure. That means that we compute the HF approximation to $\mathcal{H} = H_o + V + \varepsilon_o W$ where W is a one-electron operator for a small value of ε_o. Then, we will obtain

$$E_{\mathrm{HF}}(\varepsilon_o) = \langle \Phi_o(\varepsilon_o)|\mathcal{H}(\varepsilon_o)|\Phi_o(\varepsilon_o)\rangle \tag{34}$$

where $\Phi_o(\varepsilon_o) = \mathcal{A}(\varphi_{\varepsilon 1}(1)\varphi_{\varepsilon 2}(2)\ldots\varphi_{\varepsilon n}(n))$ is the HF wavefunction and its component orbitals are all dependent on ε_o. Furthermore,

$$f_\varepsilon(1)\varphi_{j\varepsilon}(1) = \epsilon_j(\varepsilon_o)\varphi_{j\varepsilon}(1), \tag{35a}$$

$$f_\varepsilon(1) = f_o(1) + \varepsilon_o W(1) + v_\varepsilon^{eff}(1) \tag{35b}$$

$$v_\varepsilon^{eff}(1) = \sum_{j=1}^{N} \int \varphi_{j\epsilon}^*(2)\frac{1-P_{12}}{r_{12}}\varphi_{j\epsilon}(2)d\tau_2 \tag{35c}$$

Obtaining $E_{\mathrm{HF}}(\varepsilon_o)$ at various values of ε_o will provide the perturbed energies from which the numerical derivatives may be obtained. This finite-field procedure is frequently called "coupled Hartree-Fock" (CHF) (29).

Although it does not change the conceptual content or the numerical values (if done carefully!), the much more computationally convenient analytical equivalent, called coupled *perturbed* Hartree-Fock (CPHF), can be developed by taking the derivatives *before* evaluation by expanding all the equations in perturbation theory and explicitly solving them for perturbed orbitals, $\varphi_{j\varepsilon} = \varphi_{jo} + \varepsilon_o\varphi_j^{(1)} + \cdots$, orbital energies, $\epsilon_j = \epsilon_{jo} + \varepsilon_o\epsilon_j^{(1)} + \cdots$, and using $v_\varepsilon^{eff} = v_o^{eff} + \varepsilon_o v^{eff(1)} + \varepsilon_o^2 v^{eff(2)} + \cdots$ from which $E_{\mathrm{HF}}(\varepsilon_o) = E_{\mathrm{HF}}^{(0)} + \varepsilon_o E_{\mathrm{HF}}^{(1)} + \cdots$ can be obtained.

To avoid too much of a digression, we will not present those equations here. Excellent treatments for the time-independent case are given elsewhere (27,30,31). This is also a special case for the time-dependent, TDHF, approach (11,32) discussed in Section 7. Suffice it to say that CPHF calculations are preferable to CHF, and several implementations are available.

Even at the HF level, though, we have to pay close attention to the choice of basis set, that is the (usually) contracted Gaussian atomic orbital (AO) basis used to express the MO's. It is apparent that it is essential to have a large, flexible and polarized basis set for hyperpolarizabilities. The basis must correctly describe matrix elements of the long-range operator $\hat{r}$ (i.e. $\hat{x}, \hat{y}, \hat{z}$) while the usual AO basis functions have been selected predominantly to describe the energy, which depends on shorter-range operators like $\frac{1}{r}$ and the kinetic energy operator. A basis like double zeta (DZ) would use 4s and two sets of p functions to describe the energy of a B,C,N,O,F, atom in a molecule, 2s for H. To provide adequate polarization to this basis, particularly to describe the more diffuse and directional part of the charge density, we need at least one or two sets of d-functions and probably more s and p functions. The POL+ basis (*14,33*), optimized to describe polarizabilities has a 5s3p2d distribution for B-F, and 3s2p1d for H, and would be the *minimum* recommended for most hyperpolarizability determinations. The influence of basis set is illustrated in the behavior of the components of $\underline{\alpha}$ and γ for ethylene, shown in Table III.

Table III Comparison of *Ab Initio* SCF Hyperpolarizabilities as a Function of Basis Set with Semi-empirical INDO and INDO/S for Ethylene (a.u.).

COMPONENT	SEMI-EMPIRICAL		AB INITIO SCF				EXP
	INDO	INDO/S	STO-3G	DZ	631+PD	POL+	
α_{xx}	19.9	31.7	11.45	33.6	36.0	36.4	
α_{yy}	15.9	18.1	0.75	18.0	22.9	24.6	
α_{zz}	2.8	3.7	2.84	8.6	19.4	23.1	
$\overline{\alpha}$	**12.9**	**17.8**	**5.01**	**18.4**	**26.1**	**28.0**	**28.7**
γ°_{xxxx}	-155	-2,092	-263	1,961	3,205	3,300	
γ°_{yyyy}	95	194	2	111	2,008	2,800	
γ°_{zzzz}	-6	-13	-23	64	11,303	11,900	
γ°_{xxyy}	81	25	-1	43	1,680	1,600	
γ°_{yyzz}	43	82	9	17	2,344	2,500	
γ°_{xxzz}	98	304	40	231	3,294	3,100	
$\gamma^{\circ}_{\parallel}$	**76**	**-218**	**-37**	**-241**	**6,230**	**6,500**	
$\gamma^{dcSHG}_{\parallel}$	85	-344	-42	-337	9,251	9,900	9,029 ±203
$\gamma^{THG}_{\parallel}$	96	-811	-49	-538	15,836	17,500	

Notice that a minimum STO-3G basis underestimates the HF-SCF dipole polarizability by over a factor of 5, with double zeta (DZ) still being in error by $\sim 30\%$. The essential role of polarization functions is emphasized by the 6–31G+PD, meaning additional diffuse p and d functions on C and H (*34*), and the (5s3p2d/3s2p1d) POL+ basis (*14*).

The basis set effect is amplified dramatically for γ, where *four* products of $\hat{x}$, $\hat{y}$, and $\hat{z}$ are evaluated. Note that in inferior basis sets, including STO-3G and DZ, $\gamma_{\parallel}^o$, even has the wrong sign, differing from the better converged value by at least *four* orders of magnitude! However, once a few polarization functions are included, even as in the modest 6–31G+PD basis, convergence toward the Hartree-Fock solution is relatively good. The remaining differences between $\gamma_{\parallel}^o$ and $\gamma_{\parallel}^{dcSHG}$ and $\gamma_{\parallel}^{THG}$, which means dc-induced Second Harmonic Generation and Third Harmonic Generation, the potential experimentally observed quantities, lie in the frequency dependence neglected in the static HF calculation. We will discuss that aspect later. Obviously, it, too, is numerically important in providing reliable theoretical predictions.

Semi-empirical Methods

The other numerical values use the INDO (*35*) and spectroscopically parameterized INDO/S methods (*36*), (the latter is also known as ZINDO (*37*)). Like nearly all semi-empirical methods, INDO assumes an underlying minimum Slater-Type-Orbital (STO) basis SCF description, which is close to that of STO-3G. In the INDO case, the parameters are chosen to best reproduce the minimum basis SCF results. Hence, if this were done successfully, results about on the level of STO-3G would be obtained, clearly a level far inferior to that required for hyperpolarizabilities, and this is illustrated by the observed INDO results.

INDO/S would appear to have a little better chance at obtaining reasonable values. Despite the minimum basis set description, which is clearly suspect, the spectroscopic parameterization is chosen to try to describe excitations to the low-lying excited states of molecules and their transition moments within a single excitation configuration interaction (CIS) description. After fitting parameters to known spectra of similar molecules, the method is expected to describe related molecules reliably. If this were true for *all* excited states, from the SOS formula of equation 31b, obviously the dipole polarizability would be well described as it requires only those two pieces of information. However, the low-lying states are only a few of those that contribute to the polarizability. Furthermore, as all terms have the same sign, even though those neglected might have a comparatively high excitation energy, their sum total is significant. That is why there is a large error in $\bar{\alpha}$, particularly the α_{zz} component, compared to the good *ab initio* results. Notice that INDO/S is competitive with the *ab initio* DZ description, but unlike *ab initio* methods, semi-empirical results cannot be systematically improved. You get what you get!

Once you expect to use INDO/S for $\underline{\beta}$ or γ, you now not only require transition moments between ground and excited states but *between excited states* themselves.

Such experimental information is very seldom available, much less for the plethora of possible excited states, to offer any help with parameterization.

Table III demonstrates the dramatic failure of $\gamma_{\parallel}^o$ for ethylene, where the sign is wrong and it is off by 4 to 5 orders of magnitude. The same failure happens for $\underline{\beta}$. For the small molecules, INDO/S and INDO values of $\beta_{\parallel}^o$ have the wrong sign for CO and NH_3! (See also (22) for other examples.) Consequently, considering the basis set limitations inherent to semi-empirical methods, and their general inability to describe transitions between excited states, only generalizations beyond a minimum basis description, and further and more severe parameterization explicitly for hyperpolarizabilities, should enable such methods to offer any kind of quantitatively reliable results. For design purposes, the hope is to at least reproduce the correct trends among similar molecules, and typically for only one dominant axial component rather than the whole tensor; a simpler problem.

The other widely used semi-empirical methods, like those in MOPAC (38,39) (namely MNDO, MINDO, AM1, PM3), share with INDO a minimum basis description, but parameterization is attempted to be made directly to *experimental results* like dissociation energies and other properties, instead of the minimum basis SCF values. In particular, unlike INDO/S, such approaches have not been developed *to apply* for excited states as recommended by the SOS interpretation. But even from the energy derivative viewpoint, which pertains to INDO without the "S" as well, there is still little reason to believe that such methods have much hope of reliably describing qualities as sensitive to nuances of charge distributions as are hyperpolarizabilities. Several MOPAC examples that demonstrate failures are presented in ref. (22).

Electron Correlation

Up to now, we have only considered HF level methods, *ab initio* or semi-empirical. After ensuring adequate basis sets, there are two particular corrections we need to consider: one is the frequency dependence (discussed in the next section) and the other electron correlation. Both would be essential, including their mutual coupling, to offer the definitive theoretical study for the purely electronic part of molecular hyperpolarizabilities. To initially isolate the effects, we will start with correlation corrections for static hyperpolarizabilities.

As discussed above, HF theory makes the approximation that one electron moves in an average field of *n-1* other electrons, to enable replacing the two-particle operator in the Hamiltonian by the $\sum_i v^{eff}(i)$, *one-particle* Hamiltonian. This ignores that electrons are charged species causing their motions to be *instantaneously* correlated. Clearly, the correlation of electrons bestows an additional degree of stability to the molecule, as the electrons are allowed to avoid each other, and this effect significantly contributes to the molecule's charge distribution and excited states description.

In equation 31, we derived formulas for hyperpolarizabilities based upon knowing the exact solutions to $\mathcal{H}_o$, which is the Hamiltonian in the absence of the electric field

perturbation, $\varepsilon_o W$. Such exact solutions properly include all two-electron effects in $\mathcal{H}_o$, meaning their eigenvalues and vectors are *correlated*. This should be contrasted with replacing $\mathcal{H}_o$ by the $H_o = \sum_i f(i)$ operator as employed in the HF theory. These additional effects of correlation, whether used from the energy derivative viewpoint or the SOS, can have a dramatic effect on the observed results.

We can consider various approaches to electron correlation, but those most frequently applied to hyperpolarizabilities are many-body perturbation theory (MBPT) (*4,5,40*), known in some programs as MP) and coupled-cluster (CC) theory (*7–9,14,41,42*). In MBPT, in the absence of the electric field, electron correlation corrections could be introduced with the same equations derived in equation 6–11, where $\mathcal{H}_o$ is chosen to be $H_o = \sum_i f(i)$ and the correlation perturbation $V = \sum_{i,j} \frac{1}{r_{ij}} - \sum_i v^{eff}(i)$ replaces W. Then $E^{(2)} = \langle \Phi_o | V R_o V | \Phi_o \rangle = \langle \Phi_o | V | \psi^{(1)} \rangle$. This defines MBPT(2). MBPT(2) is the simplest correlated method, consisting of the initial contribution due to double excitations from occupied to unoccupied orbitals (i.e. Φ_{ij}^{ab}). MBPT is usually applied in a given finite order n [MBPT(n)], where $n=4$ is the highest frequently used.

In the absence of an electric field, proper treatment of correlation in hyperpolarizabilities requires a double perturbation approach (*43*) where all couplings between V and $\varepsilon_o W$ are allowed (*44*), with $\varepsilon_o W$ applied in a given order to describe the particular polarizability, and V is preferably included in *all* orders. A straightforward double perturbation approach is possible, but usually in practice, the requisite coupling between V and W is handled in two other ways. The first way is by correlating states, and then adding the W perturbation; the route taken in equations 28 to 31: This will be the EOM-CC route described in Section 8. Second, we can take the viewpoint that we will first solve the HF problem, and then add correlation to that HF solution straightforwardly, except that H_o, V, Φ_o and $\psi^{(n)}$ are all dependent on ε_o. That is, we evaluate correlation corrections to the electric field perturbed Hamiltonian as $f_\varepsilon = f_o + \varepsilon_o W + v_\varepsilon^{eff}$ as in the CHF method, so

$$H_o(\varepsilon_o) = \sum_i f_\varepsilon(i) = \sum_i \left(f_o + \varepsilon_o W + v_\varepsilon^{eff} \right)(i)$$
$$V = \mathcal{H}(\varepsilon_o) - H_o(\varepsilon_o)$$
$$E(\varepsilon_o) = E_{\text{CHF}} + E^{(2)}(\varepsilon_o) + E^{(3)}(\varepsilon_o) + \cdots$$
$$E_{\text{CHF}}(\varepsilon_o) = \langle \Phi_o(\varepsilon_o) | H(\varepsilon_o) | \Phi_o(\varepsilon_o) \rangle$$

(36)

and all evaluation of correlation corrections pertain to $V(\vec{\varepsilon}_o)$; such as $E^{(2)}(\varepsilon_o) = \langle \Phi_o(\varepsilon_o) | V(\varepsilon_o) | \psi^{(1)}(\varepsilon_o) \rangle$, and, similarly, in higher orders of MBPT (*2,3,7,40*). Just as in HF theory, we have the option of doing this analytically or as a finite field.

CC theory offers a natural generalization of MBPT that sums categories of excitations to infinite order. For example, CCSD means all single and double excitations (i.e. $\Psi_{\text{CCSD}} = \exp(T_1 + T_2)\Phi_o$ where Φ_o is the independent particle

model and T_1 and T_2 are the single and double excitation operators,

$$T_2 \Phi_o = \sum_{\substack{i<j \\ a<b}} t_{ij}^{ab} \Phi_{ij}^{ab} \tag{37}$$

where occupied orbitals i and j are replaced by unoccupied orbitals a and b,

$$T_1 \Phi_o = \sum_i t_i^a \Phi_i^a \tag{38}$$

By virtue of the exponential expansion, Ψ_{CCSD} also contains triple excitations, $T_1 T_2 \Phi_o$, quadruple excitations, $T_2^2 \Phi_o$, etc., ensuring a highly correlated solution. CCSD is correct through MBPT(3) with many additional higher-order effects (9,28). The CCSD(T) model includes, in addition, a non-iterative (28) evaluation of "connected" triples, $T_3 \Phi_o = \sum_{\substack{i<j<k \\ a<b<c}} t_{ijk}^{abc} \Phi_{ijk}^{abc}$. This model, correct through MBPT(4), is demonstrably close to the basis set limit or full CI solution—the ultimate result (28). We can simply evaluate the CC results, just as described above for MBPT, by letting ψ_{CC} to be ε_o dependent, $[(\psi_{CC} = \exp(T(\varepsilon_o))\Phi_o(\varepsilon_o))$, along with $\mathcal{H}(\varepsilon_o) = H_o + V(\varepsilon_o) + \varepsilon_o W$ and $E_{CC}(\varepsilon_o) = \langle \Phi_o(\varepsilon_o) | \mathcal{H}(\varepsilon_o) e^{T(\varepsilon_o)} | \Phi_o(\varepsilon_o) \rangle]$.

Even better, because of the advantage of analytical evaluation even for the induced dipole, we might describe how that is done in CC theory. MBPT follows as a special case (18). Because $\psi_{CC}(\varepsilon_o) = \exp(T(\varepsilon_o))\Phi_o(\varepsilon_o)$ is an infinite series, we do *not* evaluate the induced dipole $\vec{\mu}(\varepsilon_o)$, as

$$\vec{\mu}(\varepsilon_o) = \langle \psi_{CC}(\varepsilon_o) | W | \psi_{CC}(\varepsilon_o) \rangle / \langle \psi_{CC}(\varepsilon_o) | \psi_{CC}(\varepsilon_o) \rangle \tag{39}$$

because the expression would have to be truncated. Instead, we can derive the form (18–28),

$$\vec{\mu}(\varepsilon_o) = \langle \Phi_o(\varepsilon_o) | (1 + \Lambda(\varepsilon_o)) e^{-T(\varepsilon_o)} W e^{-T(\varepsilon_o)} | \Phi_o(\varepsilon_o) \rangle$$
$$= \sum_{pq} \vec{r}_{pq} \gamma_{pq} \tag{40}$$

where Λ is a de-excitation operator, complementary to the excitation operator T and γ_{pq} is the element of the one-particle "relaxed density" matrix (28). Both Λ and T have to be determined from the CC equations. Subsequent finite-field differentiation relative to $\vec{\varepsilon}_o$ provides the various polarizabilities like $\frac{\partial \vec{\mu}(\varepsilon_o)}{\partial \vec{\varepsilon}_o} = \underline{\alpha}$, $\frac{\partial^2 \mu(\varepsilon_o)}{\partial \vec{\varepsilon}_o \partial \vec{\varepsilon}_o} = 2! \underline{\beta}$, etc. As mentioned, this greatly improves precision and diminishes the number of distinct $\vec{\varepsilon}_o$ values required.

Table IV shows the effect of correlation on static $\chi_{\parallel}^{(2)}(0;0,0)$ and $\chi_{\parallel}^{(3)}(0;0,0,0)$. Note the factor of 2 change for $\chi_{\parallel}^{(2)}$ of NH_3, and the order of magnitude and sign change for H_2S. Similarly, $\chi_{\parallel}^{(3)}$ changes substantially. This large correlation effect has been observed since the initial *correlated* studies of molecular hyperpolarizabilities (2,3), and makes it apparent that "predictive" *ab initio* methods for hyperpolarizabilities must include electron correlation.

Table IV Comparison of SCF and Correlated Static Hyperpolarizabilities.[c]

	$\chi_{\parallel}^{(2)a}$ $(10^{-32}$ esu/molecule)			$\chi_{\parallel}^{(3)b}$ $(10^{-39}$ esu/molecule)		
	SCF	*MBPT(2)*	*CCSD(T)*	*SCF*	*MBPT(2)*	*CCSD(T)*
H_2	-	-	-	46	50	51
N_2	-	-	-	61	78	85
CO_2	-	-	-	67	98	97
C_2H_4	-	-	-	546	630	563
CO	9.1	9.7	10.2	85	126	134
HF	-2.3	-3.0	-2.9	27	47	47
H_2O	-4.7	-7.6	-7.8	85	150	151
NH_3	-6.5	-14.0	-14.8	200	340	353
HCl	-1.3	-3.4	-3.3	213	287	295
H_2S	0.6	-4.5	-4.0	470	620	664

[a] $\beta_{\parallel}^o = (\beta_{ijj} + \beta_{jij} + \beta_{jji})/5$ with summation convention. $\chi_{\parallel}^{(2)} = \beta_{\parallel}/2$, so conversion to a.u. is 4.3195 x 10^{-33} esu/molecule/a.u.

[b] $\gamma_{\parallel}^o = (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji})/15$ with summation convention. $\chi_{\parallel}^{(3)} = \gamma_{\parallel}/6$, so conversion to a.u. is 8.395 x 10^{-41} esu/molecule/a.u.

[a] Basic sets listed in Tables VII and VIII.

Frequency Dependence

All experiments are frequency dependent, and frequency dependence introduces many different processes that become the same in the static limit.

Instead of the static field perturbation, $\vec{\varepsilon}_o \cdot \vec{W}$, consider the expansion of the induced dipole analogous to that in equation 24, for a time-dependent, oscillatory field, $\varepsilon = \varepsilon_o + \varepsilon_\omega \cos \omega t$,

$$\mu_i = \langle \Psi(\varepsilon, t)|r_i|\Psi(\varepsilon, t)\rangle$$
$$= \mu_i(o) + \alpha_{ij}(o, o)\varepsilon_{oj} + \alpha_{ij}(-\omega; \omega)\varepsilon_{oj} \cos \omega t$$
$$+ \frac{1}{2!}\beta_{ijk}(o; o, o)\varepsilon_{oj}\varepsilon_{ok} + \frac{1}{4}\beta_{ijk}(o; \omega, -\omega)\varepsilon_{\omega j}\varepsilon_{\omega k} \qquad (41)$$
$$+ \beta_{ijk}(-\omega; \omega, o)\varepsilon_{\omega j}\varepsilon_{ok} \cos \omega t + \frac{1}{4}\beta_{ijk}(-2\omega; \omega, \omega)\varepsilon_{\omega j}\varepsilon_{\omega k} \cos \omega t$$
$$+ \cdots$$

Now, in addition to the static terms we have previously considered, we obtain a number of terms that correspond to different incoming and outgoing frequencies. For

example, $\beta_{ijk}(-2\omega;\omega,\omega)$ corresponds to second harmonic generation (SHG) with incoming frequencies $\omega + \omega$ resulting in an outgoing frequency, 2ω. Similarly, $\alpha_{ij}(-\omega,\omega)$ corresponds to the dynamic polarizability, and $\beta_{ijk}(o;\omega,-\omega)$ is called optical rectification (OR), and $\beta_{ijk}(-\omega;\omega,o)$ corresponds to the electro optic Pockels effect (EOPE). If we allowed the frequencies to be different, $\beta(-\omega_1 - \omega_2;\omega_1,\omega_2)$ would correspond to two-wave mixing. Similarly, many such components occur in γ. A summary of them is shown in Table V. All become the same in the static limit; hence, *without inclusion of frequency dependence in the quantum mechanical method, we cannot distinguish between the different processes.* Obviously, we can obtain each of these quantities from an appropriate derivative,

$$\frac{\partial^2 \mu_i(\varepsilon)}{\partial \varepsilon_{\omega j} \partial \varepsilon_{\omega k}} = \frac{1}{2!}\beta_{ijk}(-o;\omega,-\omega) \qquad (42)$$

etc. Just as in the static case, that derivative can be further related to a quasi-energy derivatives (*45,46*) from the Frenkel variational principle (*11*).

Table V Representative Non-Linear Optical Processes, with Corresponding Resultant (ω_σ) and Incident ($\omega_1,\omega_2 \ldots$) Frequencies.

Non-Linear Optical Process	$-\omega_\sigma$	$-\omega_1$	$-\omega_2$	$-\omega_3$
First Static Hyperpolarizability	0	0	0	-
Second Harmonic Generation (SHG)	-2ω	ω	ω	-
Electro-Optics Pockels Effect (EOPE)	$-\omega$	0	ω	-
Optical Rectification (OR)	0	ω	$-\omega$	-
Two-Wave Mixing	$-(\omega_1+\omega_2)$	ω_1	ω_2	-
Second Static Hyperpolarizability	0	0	0	0
Third Harmonic Generation (THG)	-3ω	ω	ω	ω
Intensity-Dependent Refactive Index (IDRI)	$-\omega$	ω	ω	$-\omega$
Optical Kerr Effect (OKE)	$-\omega_1$	ω_1	ω_2	$-\omega_2$
D.C.-Induced Optical Rectification (DCOR)	0	0	ω	$-\omega$
D.C.-Induced SHG (DC-SHG)	-2ω	0	ω	ω
Electro-Optic Kerr Effect (EOKE	$-\omega$	ω	0	0
Three-Wave Mixing	$-\omega_\sigma$	ω_1	ω_1	ω_2
D.C.-Induced Two-Wave Mixing	$-(\omega_1+\omega_2)$	0	ω_1	ω_2

The first way to augment a static calculation with some measure of frequency dependence is to recognize that it may be rigorously shown (*47*) that for low

frequencies,

$$\beta(-\omega_\sigma; \omega, \omega) = \beta(o; o, o)\left(1 + A\omega_L^2 + B\omega_L^4 + \cdots\right) \qquad (43)$$

where $\omega_L = \omega_\sigma^2 + \omega_1^2 + \omega_2^2$ and A and B are unknown constants. Without an independent evaluation of A and B, the most we can conclude are the ratios of the various dispersion effects.

For example, neglecting the smaller quartic term, the SHG and EOPE values are

$$\beta(-2\omega; \omega, \omega) = \beta(o; o, o)\left(1 + 6A\omega^2\right)$$
$$\beta(\omega; \omega, o) = \beta(o; o, o)\left(1 + 2A\omega^2\right) \qquad (44)$$

showing that their ratio,

$$\frac{\beta(-2\omega; \omega, \omega)}{\beta(-\omega; \omega, o)} = \frac{1 + 6A\omega^2}{1 + 2A\omega^2} \simeq 1 + 4A\omega^2 - 8A^2\omega^4 + \cdots \qquad (45)$$

Obviously, SHG has a much greater dispersion effect than EOPE. Similarly, we have for γ,

$$\gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \gamma(0; 0, 0, 0)\left(1 + A'\omega_L^2 + B'\omega_L^4 + \cdots\right) \qquad (46)$$

The components of γ, OKE, IDRI, DCSHG and THG correspond to the values 1 plus $2A'\omega^2$, $4A'\omega^2$, $6A'\omega^2$ and $12A'\omega^2$, respectively, providing similar ratios. Obviously, the degree of dispersion follows the order THG > DCSHG > IDRI > OKE. However, we must at least know the constants to relate the various processes, particularly, to static quantities. It appears the only way at present to obtain any quantitative relationship is to evaluate the frequency dependent quantum chemical results.

The first such viable approach is the time-dependent Hartree-Fock (TDHF) method. Just as HF theory provides the simplest approach for static polarizabilities, TDHF provides the simplest *ab initio* solution to the time-dependent Schrödinger equation $\mathcal{H}(t)\Psi(t) = i\frac{\partial\Psi(t)}{\partial t}$ and, thereby, frequency dependent processes. Just as in the static case, we can impose a single determinant approximation for $\Psi(t) \approx \Phi_o(t)$, and by applying the time-dependent (Frenkel) variational/principle obtain the TDHF (or RPA) equations. The RPA equations date from long ago (*48*); however, this only pertains to excitation energies and $\underline{\alpha}$. In 1986, we made the generalization to $\underline{\beta}$, $\underline{\gamma}$, $\underline{\delta}$, $\underline{\epsilon}$, etc. and showed that *analytically* we can evaluate the frequency dependent hyperpolarizabilities from the derivatives in equation 36 in *any order* (*11*) giving ready TDHF access to hyperpolarizabilities. Others have since implemented equivalent TDHF approaches for $\underline{\beta}$ (*45*) and for $\underline{\beta}$ and $\underline{\gamma}$ (*32*). Recently, the unrestricted Hartree-Fock (open shell) generalization has been made (*49*). Figs. 1 and 2 graphically illustrate the dispersion behavior for various processes, which reflect the relative numerical proportions.
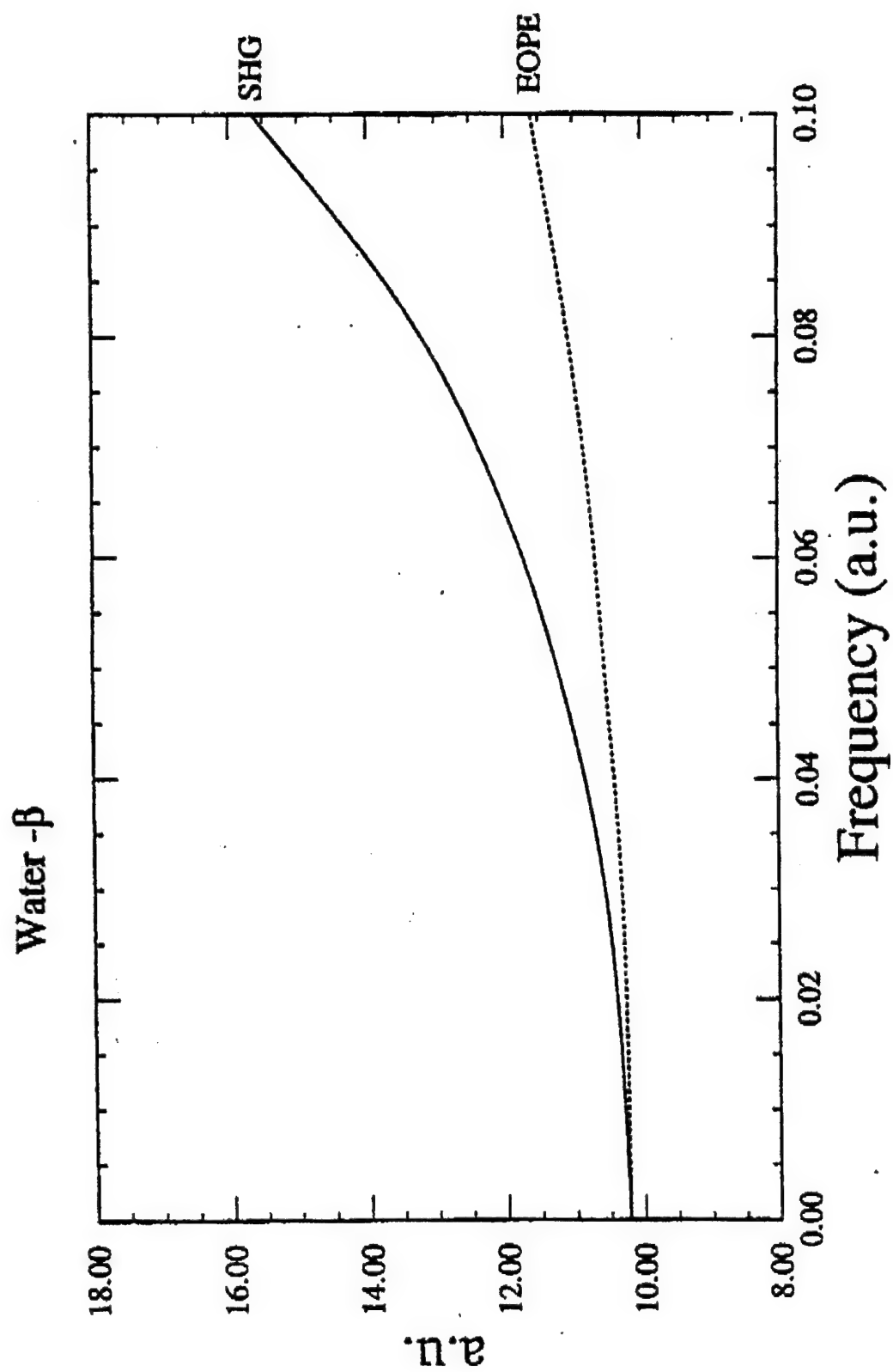
Figure 1

Figure 2

Trans Butadiene γ

THG

DC-SHG
IDRI
EOKE

Frequency(a.u.)

6.56×10^{-2}
5.25
3.94
2.62
1.31
0.00

a.u.
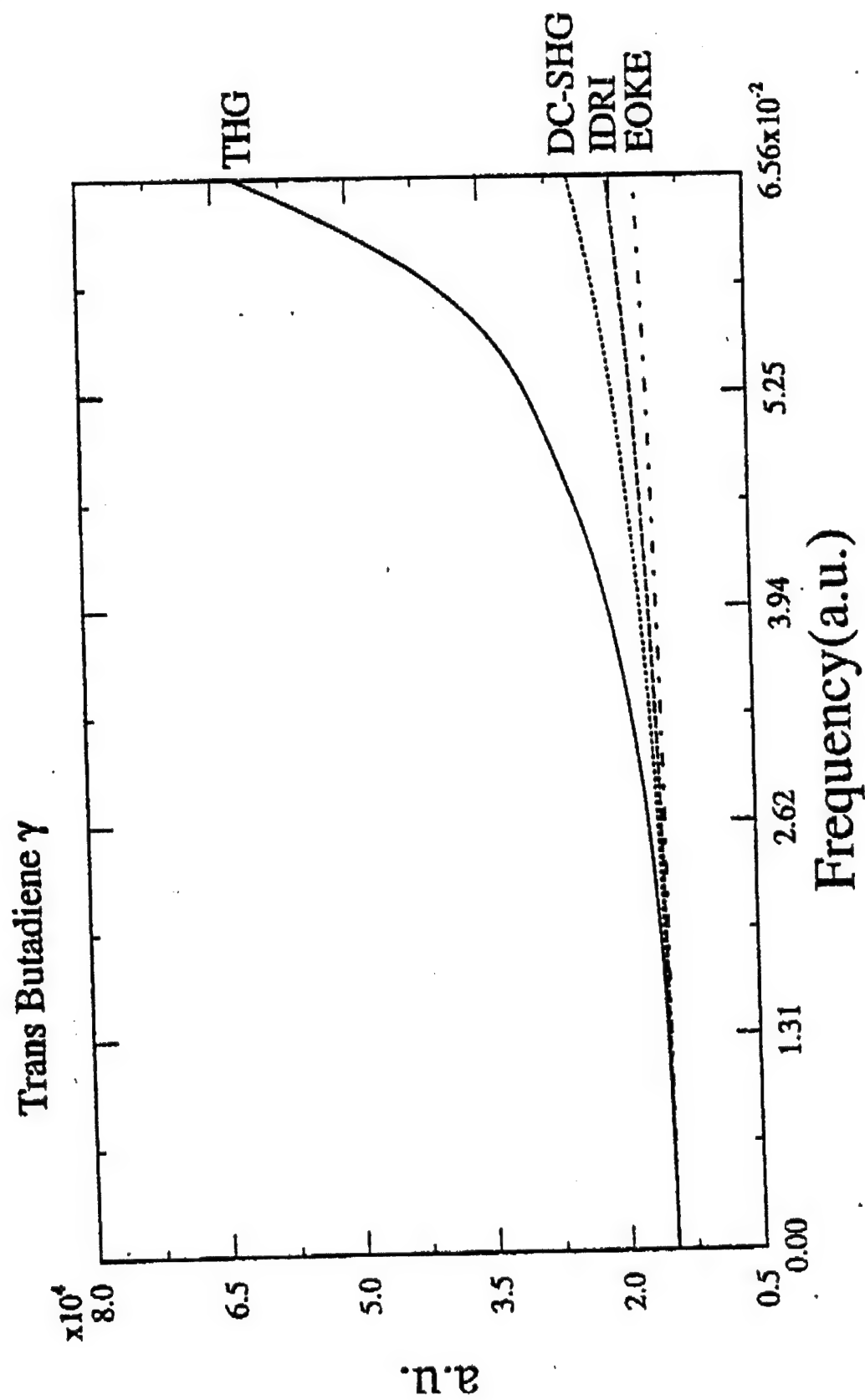
$x10^4$
8.0
6.5
5.0
3.5
2.0
0.5

24

Table VI shows the effect of dispersion in HF-level calculations of frequency dependent polarizabilities to SHG and dcSHG processes. For $\chi_{\parallel}^{(2)}$ the average change is 20% and $\chi_{\parallel}^{(3)}$ is 26%. Obviously, from the static values the other dynamic processes can show greater and lesser effects. Just as usual, we can take the derivative or SOS viewpoint in TDHF. In the latter case, the excited TDHF states are the usual RPA ones (24).

Table VI Comparison of Static and Dynamic[a] Hartree Fock Hyperpolarizabilities.[b]

	$\chi_{\parallel}^{(2)}$ (10^{-32} esu/molecule)		$\chi_{\parallel}^{(3)}$ (10^{-39} esu/molecule)	
	SCF	TDHF	SCF	TDHF
H_2	-	-	46	53.6
N_2	-	-	61	69.0
CO_2	-	-	67	76.6
C_2H_4	-	-	546	832
CO	9.1	10.5	85	102
HF	-2.3	-2.5	27	30
HCl	-1.3	-1.6	213	270
H_2O	-4.7	-5.4	85	100
NH_3	-6.5	-9.3	200	280
H_2S	0.58	0.64	470	690

[a] Values by TDHF for SHG and dcSHG at 694.3 nm.

[b] Basis sets listed in Tables VII and VIII.

At this point, we have a procedure based upon TDHF to evaluate the dispersion, and a procedure to add electron correlation to static hyperpolarizabilities. Clearly, both are critical in obtaining predictive values. Hence, guided by the fact that equations 37 and 40 are exact in the low-frequency limit, it makes sense to use a percentage TDHF dispersion correction (13) to augment static, correlated hyperpolarizabilities; namely,

$$\beta(\omega_\sigma; \omega_1, \omega_2) = \beta(0; 0, 0) \times \frac{\beta_{\text{TDHF}}(\omega_\sigma; \omega_1, \omega_2)}{\beta_{\text{HF}}(0; 0, 0)}$$

$$\gamma(\omega_\sigma; \omega, \omega_1, \omega_2) = \gamma(0; 0, 0, 0) \times \frac{\gamma_{\text{TDHF}}(\omega_\sigma; \omega, \omega_1, \omega_2)}{\gamma_{\text{HF}}(0; 0, 0, 0)}$$

(47)

By equating the percentage correction to $A\omega_L^2$ at a particular frequency, a value of A could be extracted, as well; or fitting to several different processes, A and B. In the few cases where frequency dependent *correlated* results have been obtained (20,50,51), the percentage TDHF dispersion estimate has been well supported. However, it is clear that if the TDHF=RPA result for the excitation energies are poor, then the slope

of the curve in Figs. 1 and 2 will have to eventually change to be able to approach the different asymptotic values of the excitation energy.

Using this decoupled TDHF dispersion, static correlation procedure, we obtain the results shown in Tables VII and VIII. All fall within 10% error of the experimental result except for FH, whose errors are 28% for $\chi_{\parallel}^{(2)}$ and 24% for $\chi_{\parallel}^{(3)}$; for C_2H_4, whose $\chi_{\parallel}^{(3)}$ is too large by 13.4% and N_2, and CO, whose error is a modest 11%. We have discussed FH at length elsewhere (7,14), so we will not repeat that here, except to say that we dispute the experimental values, expecting an error in its determination. Extensive studies of the convergence of FH's hyperpolarizabilities to basis set, correlation, frequency dependence and vibrational corrections (14), show no convergence to the experimental values. Instead, we propose that the correct value for $\chi_{\parallel}^{(2)}$ is $-3.6 \pm 0.3 \times 10^{-32}$ esu/molecule and $\chi_{\parallel}^{(3)}$ is $55 \pm 5 \times 10^{-39}$ esu/molecule. For the similar HCl molecule, our CCSD(T) results fall within our goal of a 10% error.

Table VII Theoretical[a] vs. Experimental[b] Hyperpolarizabilities of Molecules.

$\chi_{\parallel}^{(2)} = \frac{1}{2}\beta_{\parallel}^{SHG}$					
	TDHF	*MBPT(2)*	*CCSD*	*CCSD(T)*	*EXPERIMENT*
CO	10.5	11.2	11.4	11.7	12.9 ±1.4
HF	-2.5	-3.3	-3.2	-3.4	-4.70 ±0.41
HCl	-1.6	-4.0	-3.3	-3.8	-4.22 ±0.50
H_2O	-5.4	-8.8	-8.2	-9.1	-9.4 ±0.4
NH_3	-9.3	-20.1	-18.4	-21.2	-20.9 ±0.5
H_2S	0.6	-5.0	-3.4	-4.5	-4.3 ±0.9

[a]Value corrected for the dispersion effect at 694.3 nm using the formula,

$$\chi_{\parallel}^{(n)}(\omega) = \chi_{\parallel\text{corr}}^{(n)}(\omega = 0) \times \frac{\text{TDHF}(\omega)}{\text{TDHF}(\omega = 0)}$$

The calculations are performed with basis sets [5s3p2d] for C, N, O and F; [7s5p2d] for S; and [3s2p1d] for H. Lone-pair functions are added for HF, H_2O and NH_3. For HCl, basis is [8s6p3d1f] for Cl and [3s2p1d] for H. All molecules at experimental geometries and there is no estimate of vibrational corrections. H_2S values in lone-pair augmented basis are 1.0, -4.4, -2.8 and -3.8, respectively (14). The lone-pair basis HCl values are -1.0, -3.1, -2.6 and -3.0.

[b]Value obtained by dc-induced Second Harmonic Generation.

Table VIII Theoretical[a] vs. Experimental[b] Hyperpolarizabilities of Molecules.

$\chi_{\parallel}^{(3)} = \frac{1}{6}\gamma_{\parallel}^{dcSHG}$					
	TDHF	*MBPT(2)*	*CCSD*	*CCSD(T)*	*EXP*
H_2	54	58.2	59.3	59.3	60.5[c]
N_2	69	88.7	90.6	96	86.6 ±1.0
CO_2	77	111.5	107.9	110	111.9 ±1.3
C_2H_4	822	960	820	860	758 ±17
CO	102	151	149	160	144 ±4
HF	30	52	49	53	70 ±10
HCl	270	364	352	374	347 ±15
H_2O	100	180	170	180	194 ±10
NH_3	280	460	430	470	511 ±9
H_2S	690	910	870	930	865 ±22

[a]Value corrected for the dispersion effect at 694.3 nm using the formula,

$$\chi_{\parallel}^{(n)}(\omega) = \chi_{\parallel\,corr}^{(n)}(\omega = 0) \times \frac{\text{TDHF}(\omega)}{\text{TDHF}(\omega = 0)}$$

The calculations are performed with basis sets [5s3p2d] for C, N, O and F; [7s5p2d] for S; and [3s2p1d] for H. The lone-pair functions are added for HF, H_2O and NH_3. For HCl, basis is [8s6p3d1f] for Cl and [3s2p1d] for H. All molecules at experimental geometries and there is no estimate of vibrational corrections. The lone-pair augmented H_2S basis values are 731, 970, 930 and 980, respectively. The lone-pair basis HCl values are 274, 369, 356 and 378.

[b]Value obtained by dc-induced Second Harmonic Generation.

[c]Exact electronic value [D. M. Bishop, J. Pipin and S. M. Cybulski, Phys. Rev. **A43**, 4845 (1991)]. The experimental value of 67.2 includes a significant vibrational effect.

For C_2H_4 and N_2, we can consider more recent or rescaled experimental values (*22*). These are 76.6 ± 17 and 88.8 ± 1, respectively. This does reduce the C_2H_4 error to 12.3% and that for N_2 to 7.9%. Using the experimental results in the tables, the average error for CCSD(T) $\chi_{\parallel}^{(3)}$ is 9.4%. Excluding FH, it becomes 7.3%. Similarly, the average error for $\chi_{\parallel}^{(2)}$ is 9.4%, or 5.7% without the FH example, falling within our 10% error target objective. The various contributions are shown in Table IX. Clearly, correlation and frequency dependence are critical, and CCSD(T) is better than CCSD. However, it is gratifying that MBPT(2), which is a lot cheaper than CCSD(T), maintains about a 10% error. This level of correlation can be applied to much larger molecules (*52*) than can CCSD(T).

Table IX Percent Error of Hyperpolarizabilities at Various Levels Compared to Experiment.

	$\chi_{\parallel}^{(2)}$	$\chi_{\parallel}^{(3)}$
HF (ω=0)	57	46
TDHF (ω)	50	31
MBPT(2)	12 (9)*	9 (7)*
CCSD	19 (16)*	8 (6)*
CCSD(T)	9 (6)*	9 (7)*
*Without FH example.		

Correlated Frequency Dependent Polarizabilities

Despite the success of the decoupled correlated/TDHF results shown above, the most rigorous method would include the full coupling between correlation and dispersion. There have only been three attempts of this type for hyperpolarizabilities: a second-order [MBPT(2)=MP(2)] level method (50); a multi-configurational (MCSCF) linear response approach (51); and our EOM-CC method (20). The first two are developed from the energy (or quasi-energy) derivative viewpoint, while the latter refers, conceptually, to the SOS expressions in equation 31. In other words, EOM-CC provides excited states, $\{\psi_k^{(o)}\}$, their excitation energies, $\left(E_o - E_k^{(o)}\right)$, and generalized transition moments, $\langle\psi_k^{(o)}|r_i|\psi_o\rangle$, from which the SOS expressions could be formally constructed. That form is particularly convenient, since frequency dependence can be trivially added to such an SOS expression. For example, for some frequency ω,

$$-\alpha_{ij}(-\omega;\omega) = \left\{ \sum_{k\neq o} \frac{\langle\psi_o|r_i|\psi_k^{(o)}\rangle\langle\psi_k^{(o)}|r_j|\psi_o\rangle}{\omega_k + \omega} + \frac{\langle\psi_o|r_j|\psi_k^{(o)}\rangle\langle\psi_k^{(o)}|r_i|\psi_o\rangle}{\omega_k - \omega} \right\} \quad (50)$$

When $\omega = E_o - E_k^{(o)} = \omega_k$, we have a pole, whose residue is the dipole strength $\langle\psi_o|r_j|\psi_k^{(o)}\rangle\langle\psi_k^{(o)}|r_i|\psi_o\rangle$.

The basic idea of EOM is very simple (53). Consider the solutions to the Schrödinger equation for an excited state, ψ_k^o and for the ground state, ψ_o,

$$\mathcal{H}_o\psi_o = E_o\psi_o \quad (51a)$$

$$\mathcal{H}_o\psi_k^{(o)} = E_k^{(o)}\psi_k^{(o)} \quad (51b)$$

Now we will choose to write $\psi_k^{(o)} = \mathcal{R}_k\psi_o$, where $\mathcal{R}_k$ is an operator that creates excitations from ψ_o. If we limit ourselves to single and double excitations, we

will define an EOM-CCSD approximation. Inserting the excited state expression into equation 49b, multiplying equation 49a by $\mathcal{R}_k$ from the left and subtracting, we obtain

$$(\mathcal{H}_o \mathcal{R}_k - \mathcal{R}_k \mathcal{H}_o)\psi_o = \left(E_k^{(o)} - E_o \right) \mathcal{R}_k \psi_o \tag{52a}$$

$$[\mathcal{H}_o, \mathcal{R}_k]\psi_o = \omega_k \mathcal{R}_k \psi_o \tag{52b}$$

with the commutator between $\mathcal{H}_o$ and $\mathcal{R}_k$, [i.e. $(\mathcal{H}_o, \mathcal{R}_k)$], expression gives the "equation-of-motion," from the obvious connection with Heisenberg's form. To introduce CC theory, we simply choose for the correlated ground state, $\psi_o = \psi_{CC} = \exp(T_1 + T_2)\Phi_o$. As $\mathcal{R}_k$ and T_n are all excitation operators, $[\mathcal{R}_k, T_n] = 0$, and we can commute the operators to give,

$$[e^{-T}\mathcal{H}_o e^T, \mathcal{R}_k]\Phi_o = [\bar{\mathcal{H}}_o, \mathcal{R}_k]\Phi_o = \omega_k \mathcal{R}_k \Phi_o \tag{53}$$

recognizing that

$$\hat{\mathcal{R}}_k \Phi_o = r_o + \sum_{i,a} r_i^a \Phi_i^a + \sum_{\substack{i<j \\ a<b}} r_{ij}^{ab} \Phi_{ij}^{ab} \tag{54}$$

the coefficients $\{r_i^a, r_{ij}^{ab}\}$ are to be determined by the matrix equation,

$$\bar{\mathbf{H}} \mathbf{r}_k = \mathbf{r}_k \omega_k \tag{55}$$

Since $\bar{\mathcal{H}}_o$ is not Hermitian, we also have left-side eigenvectors, $\Phi_o \mathcal{L}_k$, which unlike $\mathcal{R}_k \Phi_o$, correspond to de-excitation processes. The $\mathcal{L}_k$ and $\mathcal{R}_l$ states are biorthogonal, $\langle \Phi_o | \mathcal{L}_k \mathcal{R}_l | \Phi_o \rangle = \delta_{kl}$. Their matrix equation is, $\mathbf{l}_k \bar{\mathbf{H}}_o = \omega_k \mathbf{l}_k$. The corresponding generalized transition moments are obtained from $\langle \Phi_o | \mathcal{L} e^{-T} r_i e^T \mathcal{R}_l | \Phi_o \rangle = \langle \Phi_o | \mathcal{L}_k \bar{r}_i \mathcal{R}_l | \Phi_o \rangle$. Notice $\langle \Phi_o | \mathcal{L}_k \bar{r}_i \mathcal{R}_l | \Phi_o \rangle \neq \langle \Phi_o | \mathcal{L}_l \bar{r}_i \mathcal{R}_k | \Phi_o \rangle$ since the operator $\bar{r}_i$ is not Hermitian. The observable quantity, however, is the dipole strength (the product), *not* the transition moment itself.

Now if we return to equation 48, in terms of EOM-CC solutions, we have

$$-\alpha_{ij}(-\omega; \omega) = \sum_{k \neq o} \left\{ \frac{\langle \Phi_o | (1+\Lambda)\bar{r}_i \hat{\mathcal{R}}_k | \Phi_o \rangle \langle \Phi_o | \mathcal{L}_k \bar{r}_j | \Phi_o \rangle}{\omega_k + \omega} \right.$$
$$\left. + \frac{\langle \Phi_o | (1+\Lambda)\bar{r}_j \mathcal{R}_k | \Phi_o \rangle \langle \Phi_o | \mathcal{L}_k \bar{r}_i | \Phi_o \rangle}{\omega_k - \omega} \right\} \tag{56}$$

Notice, we used the fact that $\langle \Phi_o | \mathcal{L}_o = \langle \Phi_o | (1+\Lambda)$, which is the same Λ operator introduced in equation 40, and that $\mathcal{R}_o = 1$.

Though informative in this form, we would still have to truncate the SOS. To avoid any such truncation, we need to recognize that all EOM-CC states are ultimately represented in terms of their underlying single and double excitations, i.e.

29

the expression in equation 54. If we collectively represent all $\{\Phi_i^a; \Phi_{ij}^{ab}\}$ as $|\mathbf{h}\rangle$, it may be shown (19) that equation 48 may be written as

$$
\begin{aligned}
-\alpha_{ij}(-\omega; \omega) = &(\langle\Phi_o|(1 + \Lambda)(\bar{r}_i - \langle\bar{r}_i\rangle)T_\pm^{(j)}|\Phi_o\rangle \\
&+ \langle\Phi_o|(1 + \Lambda)(\bar{r}_j - \langle\bar{r}_j\rangle)T_\pm^{(i)}|\Phi_o\rangle)
\end{aligned}
\tag{57}
$$

where $\langle\bar{r}_i\rangle$ is the generalized expectation value like that in equation 40, without ε_o dependence). Analogous to ordinary perturbation theory [equations 28 to 30], the first-order perturbed correlated wavefunction is given in terms of the resolvent operator matrix $\mathbf{R}_o$,

$$
\langle\mathbf{h}|T_\pm^{(j)}|\Phi_o\rangle = \langle\mathbf{h}|E_{\text{CC}} \pm \omega - \bar{\mathbf{H}}_o|\mathbf{h}\rangle^{-1}\langle\mathbf{h}|\bar{r}_j|\Phi_o\rangle = \mathbf{R}_o\langle\mathbf{h}|\bar{r}_j|\Phi_o\rangle
\tag{58}
$$

In practice, instead of inversion, we solve the *very large* linear equation,

$$
\langle\mathbf{h}|E_{\text{CC}} \pm \omega - \mathcal{H}_o|\mathbf{h}\rangle\langle\mathbf{h}|T_\pm^{(j)}|\Phi_o\rangle = \langle\mathbf{h}|\bar{r}_j|\Phi_o\rangle
\tag{59}
$$

at a given value of ω for the $T_\pm^{(1)}$ coefficients. Hence, we can evaluate the SOS dynamic polarizability *without any truncation (19,20)*!

From the above evaluation of $\alpha(-\omega; \omega)$, we can obtain the hyperpolarizabilities for the optical Kerr effect (OKE) as follows. $\beta(-\omega; \omega, o)$, sometimes also called the EOPE, is the second-order hyperpolarizability obtained from a Kerr effect experiment, while the EOKE corresponds to $\gamma(-\omega; \omega, o, o)$. Because of the static fields in both processes, we are able to obtain $\beta(-\omega; \omega, o)$ and $\gamma(-\omega; \omega, o, o)$ from finite-field differentiation of $\alpha(-\omega; \omega)$. That is, we evaluate $\alpha_{ij}(-\omega; \omega)$ analytically, using equations 56 and 57, where we use the perturbation $\vec{\varepsilon}_o \cdot \vec{r}$ instead of just $\vec{r}$. Then we obtain $\alpha(-\omega; \omega_o, \varepsilon_o)$, from which

$$
\beta^k(-\omega; \omega, o) = \frac{\partial\alpha(-\omega; \omega; \varepsilon_o)}{\partial\varepsilon_o}
\tag{60a}
$$

$$
\gamma^k(-\omega; \omega, o, o) = \frac{\partial^2\alpha(\omega; \omega; \varepsilon_o)}{\partial\varepsilon_o^2}
\tag{60b}
$$

Results are shown in Table X for NH_3 and trans-butadiene as a function of frequency, for EOM-CC and TDHF. The usual very large effect of correlation accounts for the much larger magnitude for the EOM-CC values, while the comparative dispersion values are indicated as the percent dispersion in parentheses. For NH_3, there is about 10% greater dispersion as measured by EOM-CC compared to TDHF at the high frequencies (0.1 a.u.), but not at the low frequency (0.0656 a.u.) value used in the dcSHG experiments we previously described. For butadiene, the percentage dispersion is close, but the slightly smaller value helps to reduce our calculated values to be in somewhat better agreement with experiment. Unlike most other molecules we have studied, TDHF results for ethylene and butadiene are fortuitously close to experiment, while correlation hurts the agreement. The origin of this is not yet clear,

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but the fact that the correlated dispersion is smaller than that for TDHF could be ascribed to the TDHF=RPA excitation energies being too low, causing the curve in Fig. 2 to rise too quickly to approach the wrong asymptotic values. For multi-bonded molecules like ethylene and butadiene, the restricted HF result is not triplet stable, although this only prohibits RPA from correctly describing triplet excited states, the RPA singlet excitations tend to be lower than experiment; contrary to that for most systems. This may partially account for TDHF giving higher percentage dispersion corrections.

Table X Kerr Effect Tensors for NH_3 and C_4H_6 Calculated at Different Frequencies (in au).[a]

Frequency (au/nm)	0	0.043/1060	0.0656/694.3	0.1/455.6
$NH_3{}^a$ (POL+)				
β^k [b]	-35.9 -14.7	-	-41.5 (15.7%) -16.6 (12.7%)	-51.5 (43.5%) -19.7 (33.8%)
γ^k [c]	4136.63 2404.99	-	4703.00 (13.7%) 2646.36 (10.0%)	5711.56 (38.1%) 3039.95 (26.4%)
$C_4H_6{}^d$ (631G+PD)				
$\gamma_{xxxx}(-\omega;\omega,0,0)$	41200 23514	44000 (6.9%) 25571 (8.7%)	48100 (16.8%) 28733 (22.2%)	-
γ^k	20700 14812	21900 (5.7%) 15794 (6.6%)	23700 (14.1%) 17277 (16.7%)	-

[a] The numbers in upper and lower rows are evaluated by EOM-CC and TDHF, respectively. x is the C_3 molecular axis.

[b] $\beta^k = \frac{3}{10}(3\beta_{ixi} - \beta_{iix})$

[c] $\gamma^k = \frac{1}{10}(3\gamma_{ijij} - \gamma_{iijj})$

[d] The numbers in upper and lower rows are evaluated by EOM-CC and TDHF, respectively. The x component corresponds to the longitudinal molecular axis and the z component is perpendicular to the molecular plane.

We have not discussed vibrational contributions to predictive studies of hyperpolarizabilities, but these can sometimes be important (21). In equation 48, e.g., we could have contributions from all vibronic states indexed by k, instead of just the electronic ones. For an optical frequency, ω, which is much greater than a vibrational energy, such slight changes in $E_k^{(o)}$ would have negligible numerical value. However, for NLO processes that involve static fields, the SOS formulas will have some denominators without an additional large ω value, causing the vibronic changes in

$E_k^{(o)}$ to be more significant to the final result. The vibrational energy levels can be substantially perturbed by such an electric field as we have shown numerically for FH and H_2 (10). Because of the static fields in OKE, this is an example where attention needs to be paid to such effects. Assisted by a determination of β_k^v and γ_k^v (54), we can extract from our calculations predictions for $\beta^k = \beta_k^{el} + \beta_k^v$ and $\gamma^k = \gamma_k^{el} + \gamma_k^v$ that could be compared with experiment. For NH_3, MBPT(2) values for β_k^v and γ_k^v are 3.8 and 135 a.u. at 0.07 a.u. This suggests that $\beta^k \approx -36$, $\gamma^k \approx 4800$ at $\omega = 0.0656$. For butadiene, there is a larger (SCF), $\gamma^v = 1395$ to 1762 a.u., [55] giving $\gamma^k \approx 25000$.

Future Extensions

There are a couple of fairly obvious extensions that should be made in future theoretical work for NLO material design. In the short term, we obviously need to generalize analytical frequency dependent EOM-CC for all the components of $\underline{\beta}$ and $\underline{\gamma}$. Also, considering the good accuracy of MBPT(2) level correlation, purely analytical, frequency dependent versions for $\underline{\beta}$ and $\underline{\gamma}$ are strongly recommended, that should remove the current constraints (50). Other routes to partitioned EOM-CC approximations that are operationally second-order, can be envisioned (56) and should be pursued.

Obviously, it would also be nice to be able to treat hyperpolarizabilities for molecules in solution. Several such solvation methods, ranging from continuous reaction fields to more detailed solvation models are becoming available (57). These should help in sorting out the large discrepancies among results from solvation experiments (EFISH) (58).

In the longer term, we need theoretical methods comparable to that presented for small molecules that are applicable to extended, polymeric systems (59). The first such approaches should employ periodicity, with future extensions directed at the inclusion of impurity effects.

Today, it is not possible to use analytical gradient techniques with correlation to move atoms around in polymers, as it is for molecules. Nor, are there the quality *ab initio* methods for band gaps, and excited states, and polarizabilities as there are for molecules. Clearly, developing the tools for rational NLO polymer design should have a high priority.

As current high-level *ab initio* methods will eventually encounter limitations, even for periodic systems, simplified techniques should be pursued, simultaneously. The questionable reliability of semi-empirical MO theory suggests that a better "semi-empirical" approach is likely to be offered by modern density functional theory (DFT). Although DFT has a rigorous base, in application it is semi-empirical. Such methods are well known for extended systems, and have decided computational advantages, compared to *ab initio* correlated methods, but they have not yet been demonstrated to provide comparable results to those presented in this chapter. In fact, one paper says that Kohn-Sham DFT does not work for molecular hyperpolarizabilities (60). We have considered other DFT variants, however, and find that competitive results can be

obtained (*61*). The significant computational advantages of DFT make this a profitable area for study. Frequency dependent approaches need to be developed, however. Also, the conventional wisdom is that DFT does not admit treatments for excited states. Exploiting the equivalent derivative viewpoint should avoid any such formal restrictions for polarizabilities. Also, the ultimate limitation of applied DFT methods, like semi-empirical MO methods, is that there is no way to systematically converge to the exact result. New methods that combine elements of *ab initio* correlated theory with DFT methods will be forthcoming and might alleviate this failing.

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1   R.J. Bartlett and H. Sekino, "Can Quantum Chemistry Provide Reliable Hyperpolarizabilities?", in *Nonlinear Optical Materials: Theory and Modeling*, ed. S. Karna, pg. 23 (1996), American Chemical Society. (This is the text of the Final Report)

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Invited Presentations

October 1995 — "An Introduction to Coupled-Cluster Methods and Other Correlated Approaches", Postec University, Pohang, Korea.

October 1995– "Coupled-Cluster Theory as a Unified Approach to Molecular Spectroscopy: Vibrational, Electronic, and NMR,",Korean Chemical Society, Pusan, Korea

September 1995 — "Equation-of-Motion Coupled-Cluster Method for Excited, ionized and Electron-Attached States", Molecular Quantum Mechanics: Methods and Applications Conference, Cambridge University, England.

May 1995 — "Equation of Motion Coupled Cluster Methods for Excited, Ionized and Electron-Attached States," Pople Symposium, Northwestern University, Evanston, IL

October 1994 — "Coupled Cluster Theory as a Unified Approach to Molecular Spectra," Workshop on Non-Perturbative Many Body Methods (From Quantum Field Theory to Chemistry)," Bad Honnef, Germany

August 1994 — "Correlated Frequency Dependent Hyperpolarizabilities: The Equation-of-Motion Coupled-Cluster Method," 208th American Chemical Society National Meeting, Washington, DC

June 1994 — "Coupled Cluster Theory as a Unified Approach to Molecular Spectra," 8th International Congress of Quantum Chemistry, Prague, Czech Republic

June 1994– "Properties in Coupled Cluster Theory," 8th International Congress of Quantum Chemistry Satellite Meeting, Bratislava, Slovakia

December 1993 — "Quantum Chemistry of Relevance for the US Department of Defense," Stockholm, Sweden

December 1993 — Symposium on Molecular Interactions, Aarhus University, Aarhus, Denmark

November 1993 — Air Force/Navy Nonlinear Optical Polymers Conference, Washington, DC

August 1993 — 206th National Meeting of the American Chemical Society, Chicago, Illinois

July 1993 — International Academy of Quantum Molecular Science, Menton, France

June 1993 – First Congress of the International Society for Theoretical Chemical Physics, University of Girona, Girona, Spain

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